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INVESTIGATION OF O_3F_2 AND THE HYPERGOLIC BIPROPELLANT $LH_2/LO_2:O_3F_2$

by

A. B. Amster, E. L. Capener, L. A. Dickinson, and J. A. Neff

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

TASK ORDER CONTRACT NO. NASr-49(00) [LeRC(01)]

STANFORD RESEARCH INSTITUTE

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FINAL REPORT

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Task Order Contract No. NASr-49(00) LeRC(01)
Technical Management
NASA Lewis Research Center
Cleveland, Ohio
Advanced Technology Office
G. Dale Roach

STANFORD RESEARCH INSTITUTE
MENLO PARK, CALIFORNIA

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ABSTRACT

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The properties of ozone fluoride and its solution in liquid oxygen have been studied. Neat ozone fluoride has been shown to be nondetonable at a diameter of one inch. The solubility relationship of ozone fluoride in liquid oxygen versus temperature has been determined.

Ignition studies made by using quartz and steel combustion chambers (500 lb. thrust) have shown that hypergolic ignition occurs between hydrogen and liquid oxygen containing 0.095% ozone fluoride. Both a single-element triplet injector and a multielement coaxial stream injector were studied.

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I SUMMARY

Solutions of ozone fluoride in liquid oxygen were studied for use as a hypergolic additive to the liquid oxygen/liquid hydrogen propellant system. Ozone fluoride is a molecule which is thermally unstable above 110°K; it is, however, extremely reactive with many materials and it is a powerful oxidizing agent.

The solubility of O_3F_2 in liquid oxygen and the stability of the solutions were investigated. Detonability of neat O_3F_2 and the phenomena accompanying ignition of O_3F_2/LOX solutions with hydrogen were studied.

The results obtained have shown that O_3F_2 is soluble to the extent of 0.095% by weight at 90°K and 1-atm pressure. This solution has been shown to be hypergolic with hydrogen gas in a triplet injector. Satisfactory ignition was also achieved by using a multielement coaxial stream injector fed with liquid hydrogen and LOX/O_3F_2.

The detonability experiments have shown that no detonation hazard exists at diameters of less than one inch; consequently no detonation problems are to be anticipated in its synthesis and use.* The storability experiments have shown that the 0.095% solution of O_3F_2 in LOX is stable for upwards of one month at 90°K.

The studies completed in this investigation have confirmed that ozone fluoride can be used to obtain hypergolic ignition in rocket engines which use liquid hydrogen as the fuel. The hazards of its use are shown to be minimal, and it is considered that slight modification of existing "cryogenic" procedures will enable LOX:O_3F_2 to be handled successfully on the scale appropriate to the large rocket engines now being developed.

*These experiments were designed to detect only Von Neumann detonations and not lower velocity explosions which may be equally hazardous.

II INTRODUCTION

The liquid bi-propellant combination, liquid hydrogen and liquid oxygen, is being used in many rocket engines now under development for space vehicles. The reliability and utility of these engines could be enhanced if the propellant combination were hypergolic.

In previous studies at the Institute and elsewhere the existence of ozone fluoride (O_3F_2) had been established and methods for its synthesis characterized. Investigations had shown that O_3F_2 was a powerful oxidizing agent and that its saturated, but dilute, solution in liquid oxygen was hypergolic with many reducing agents.

This present investigation was concerned primarily with characterizing the properties of ozone fluoride and of its solution in liquid oxygen. Particular attention was paid to (1) ascertaining, and eliminating, the hazards associated with the use of ozone fluoride, (2) elucidating the conditions for satisfactory hypergolic ignition of the LH_2/LOX:O_3F_2 bi-propellant in a small combustion chamber.

Many unique problems arose in studying O_3F_2 because its liquid oxygen solution is thermally unstable above 110°K and it is also photochemically unstable. A new procedure for measuring detonability at very low temperatures and a new technique for solubility determination were developed.

Because of the abnormal chemical reactivity of O_3F_2 normal chilling procedures could not be used; this caused problems in the small combustion chamber ignition studies.

III PREPARATION OF O_3F_2

Most of the O_3F_2 used for these investigations was prepared by the method of Kirshenbaum and von Grosse[1] modified as described in Reference 2. A small quantity was also produced by using a newly designed multiple reactor with three pair of electrodes, Fig. 1. During periods of up to two hours the new reactor produced O_3F_2 at a rate of 7-10 cc/hour compared to 2-3 cc/hour with the conventional reactor. For longer periods this rate probably could not be maintained unless, as is done with the smaller unit, product is periodically removed. This can be accomplished, while the reactor is still functioning, by replacing the liquid N_2 bath with LOX for 5-10 minutes while the O_3F_2 melts and drains from the reactor walls. Single reactors have been so operated successfully for 12-16 hours with good results.

The oxygen used for the synthesis was obtained from Matheson Company (Extra Dry Grade, purity 99.6% min.), and the fluorine, from Allied Chemical Company (typical analysis 98%, major impurity HF).

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[1] A. D. Kirshenbaum and A. V. Grosse, J. Am. Chem. Soc. 81, 1277 (1959)

[2] A. B. Amster, J. A. Neff, and A. J. Aitken, Final Report, SRI Project PRU-3652, Contract NASr-38, 1962

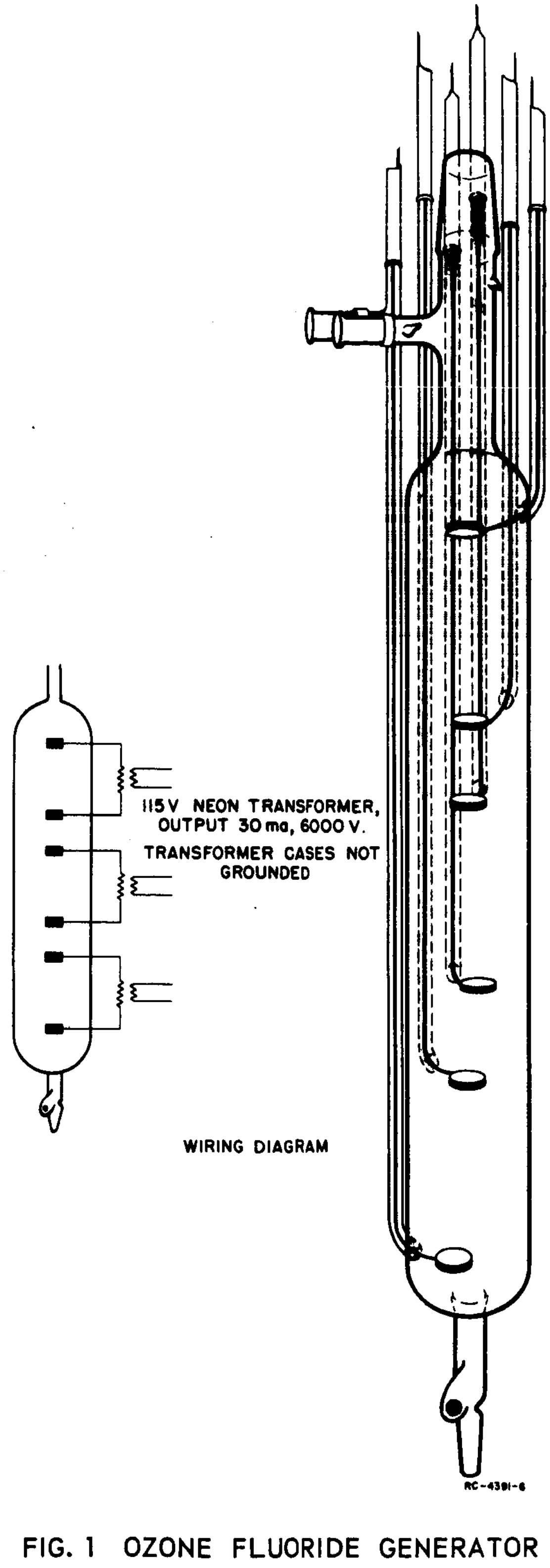

FIG. 1 OZONE FLUORIDE GENERATOR

IV SOLUBILITY OF O_3F_2 IN LIQUID OXYGEN

A. Introduction

Ozone fluoride, O_3F_2, has a number of unusual characteristics: it is photosensitivie, is unstable above 110° K, and renders liquid oxygen (LOX) hypergolic with many fuels, including liquid hydrogen. Because of this last quality, O_3F_2 has potential as a propellant additive and, for this reason, a need exists for a precise determination of the solubility of the material in LOX from 77-100° K. Indirect measurements have been made at 77° and at 90° K;[1] confirmation of the reported results and extension of the measurements to higher temperatures were desired. This is a report of the apparatus and procedures used and the results obtained from research having such a goal. To our knowledge this is the first time that a direct measurement has been made of the very slight solubility of such an intractable material within the stated temperature range.

B. Experimental

1. Apparatus and Procedure

The method involves quantitative recovery of the O_3F_2 dissolved in a large measured volume of saturated solution; this is accomplished by careful evaporation of the solvent at a temperature at which the solute vapor pressure is insignificant. The amount of residual O_3F_2 is determined by decomposing to fluorine and oxygen and either (1) measuring the total volume and pressure of gas produced or (2) analyzing for fluorine by mercury absorption.

In use the solubility apparatus is placed within a well suspended from the floor of the dry box. A schematic drawing of the flow system is given in Fig. 2 and of the cryostat and contents in Fig. 3. A perspective drawing of the solubility apparatus appears in Fig. 4.

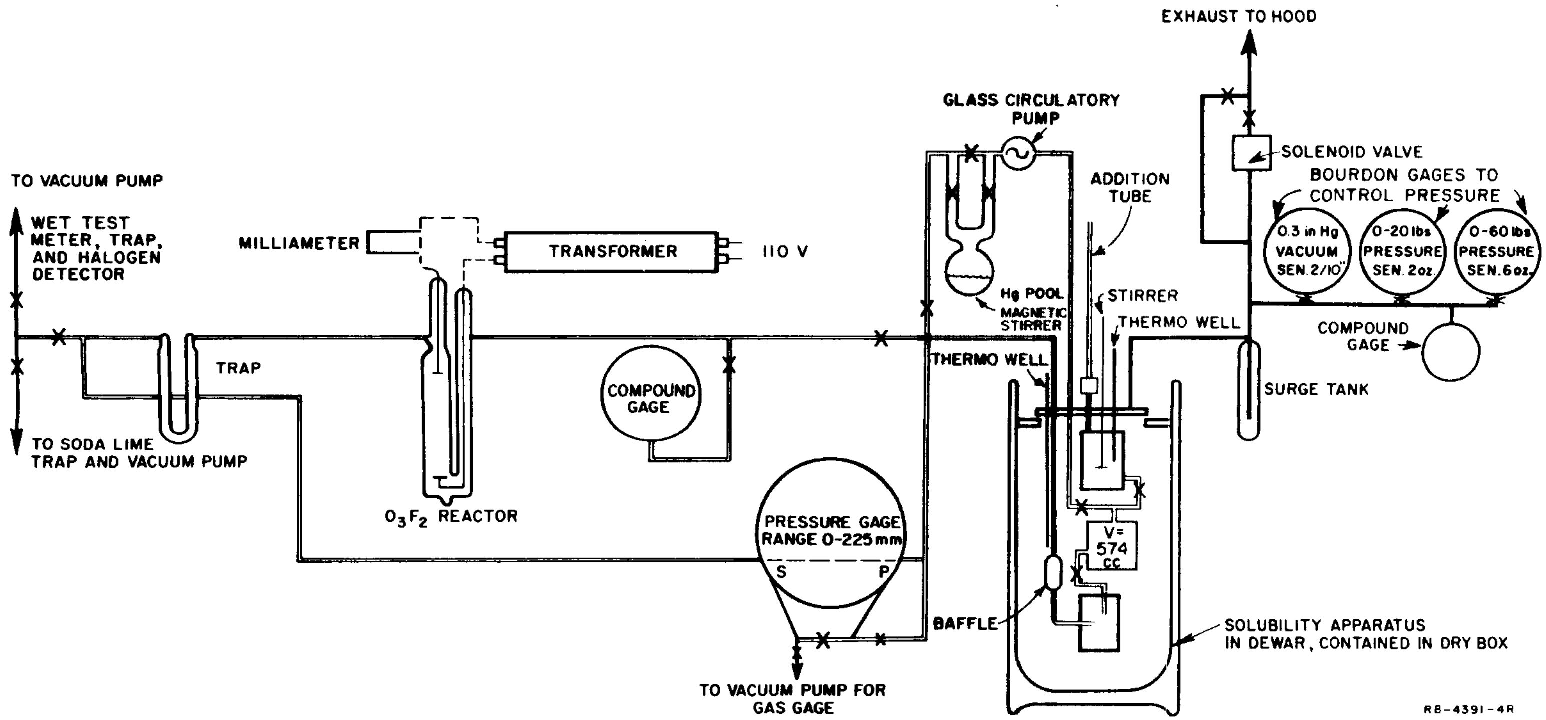

FIG. 2 SCHEMATIC — FLOW SYSTEM

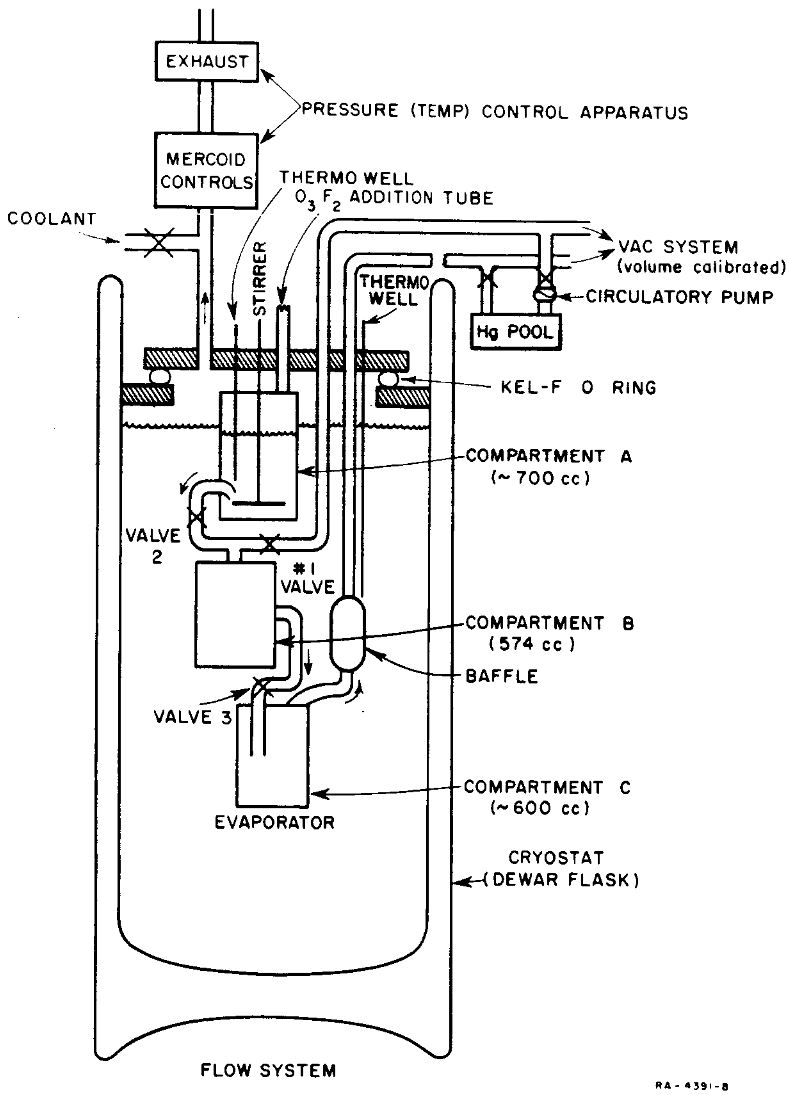

FIG. 3 SCHEMATIC — CRYOSTAT CONTENTS

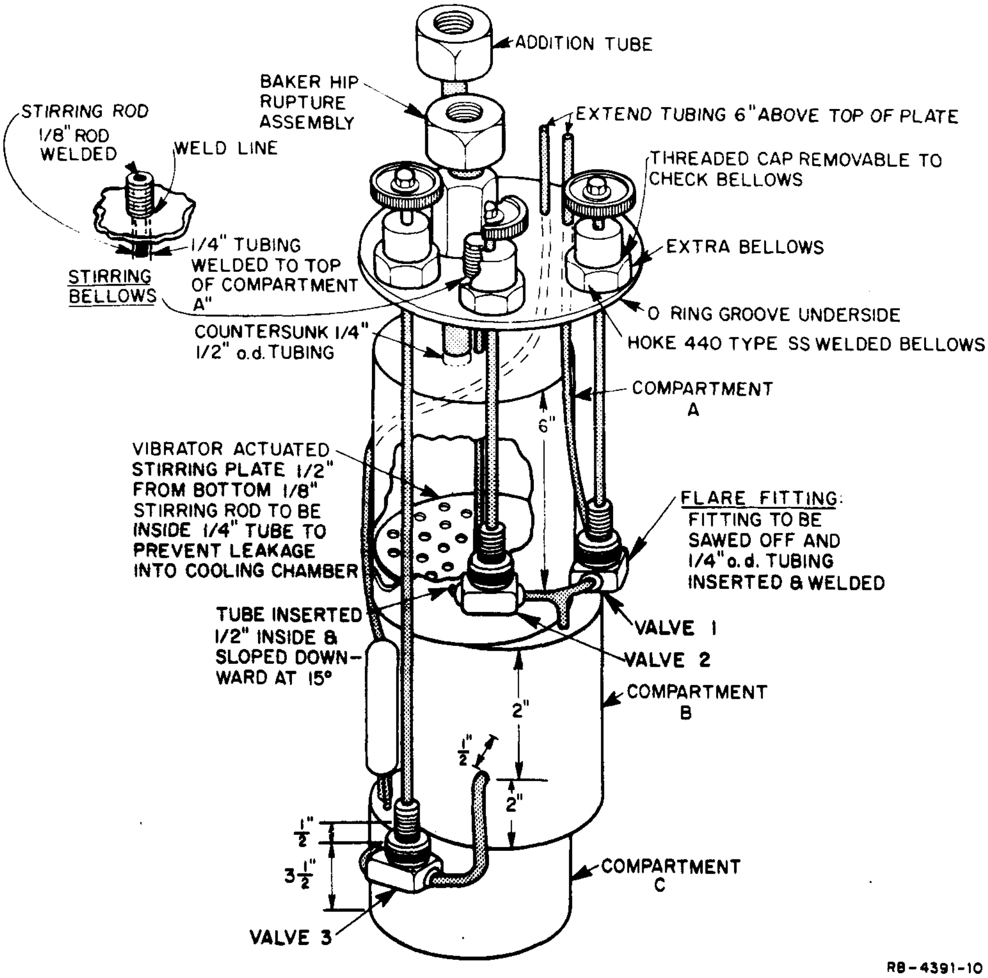

FIG. 4 PERSPECTIVE — CRYOSTAT CONTENTS

The following procedure was used to make measurements: Coolant (LOX or liquid nitrogen depending upon the desired temperature) was transferred directly from the storage container through dry copper lines to the cryostat in the dry box. Next, with valves 1, 2, and 3 closed (Fig. 3), Compartment A (~700 cc) was almost filled with liquid oxygen (USP) and an excess of O_3F_2 was added through the addition tube by using a LOX-cooled funnel. The coolant vessel was disconnected from the apparatus, and both addition tubes were closed with Teflon rupture disc assemblies (not shown).

Because of heat transfer through the cryostat walls the coolant slowly warmed under its own vapor pressure to a total pressure determined and regulated by the setting of the "Mercoid" pressure control and auxiliary valve. By this means the bath temperature and therefore the solution temperature were maintained to ±0.1°K for periods longer than 1/2 hour.

O_3F_2 is only slightly soluble in and is denser than LOX; consequently vigorous stirring was required. The mixture was stirred for at least 1/2 hour by vigorous up-and-down movement of the perforated stirrer plate actuated through a flexible bellows.

The O_3F_2 solution was then assumed to be saturated, stirring was stopped, and the excess O_3F_2 was allowed to settle to the bottom of Compartment A below the inlet of the line from A to B.* Inasmuch as the inlet slopes towards A, droplets of O_3F_2 in the connecting tube returned to A. Compartment B (574 cc), previously evacuated, was filled by opening valve No. 2; meanwhile A was pressurized with oxygen to 5-10 psi above equilibrium pressure through a fitting (not shown) on the O_3F_2 addition tube. At this stage a saturated solution of O_3F_2 in LOX had been prepared at the desired temperature.

Valve No. 2 was then closed, the cryostat vented to the atmosphere, and sufficient liquid nitrogen added to the LOX in the cryostat to reduce its temperature below 80°K where O_3F_2 has an insignificant vapor pressure.

Elimination of LOX from the solution was initiated by slowly opening valve No. 3 to the evaporator (~500 cc) and other valves from Compartment C to the vacuum pump. The inlet from No. 3 extends approximately halfway into C, so the latter could not fill more than halfway. To minimize splashing and loss of solute, the evaporation was conducted very slowly. Further, any droplets caught in the exhaust were trapped in the enlarged baffle (Fig. 3) and returned to C. The exhaust from the vacuum pump flowed through a calibrated wet test meter to measure the volume of cooled oxygen. This value was compared to that calculated from the amount of LOX originally contained in

*Time allowed for settling was shown to be adequate by previous work carried out at SRI.

the mixing chamber. The comparison was not very accurate, but gross discrepancies were assumed to be an indication of component failure and a basis for rejection of results.

After about 3-1/2 hours the evaporation was complete, and the pressure in B and C dropped abruptly from about 100 mm to less than 1 mm. The valve to the vacuum pump was closed, Compartment A was vented to the atmosphere, and the cryostat was removed to allow the apparatus to attain ambient temperature and the O_3F_2 to dissociate.

Next valve No. 1 was opened, and the O_2 + F_2 mixture expanded into the evacuated volume-calibrated loop of the vacuum system, which includes the pressure gauges, reactor, trap, Hg pool, etc. (see Fig. 2). The pressure in this volume was measured.

Fluorine was then removed by circulating the gaseous mixture over the stirred mercury pool. When the pressure was constant for at least 1 hour this process was assumed complete, and the final pressure was noted. The amount of O_3F_2 remaining after removal of the LOX was calculated from the pressure of the resultant O_2 - F_2 gas mixture and, except for solutions prepared at 77°K, from the pressure drop caused by removal of the fluorine.

2. Control Experiments

(a) One experiment was conducted in which every operation except the addition of O_3F_2 was performed as in a normal solubility determination. Approximately 0.9-mm Hg pressure was developed by warming the chamber subsequent to solvent removal. All calculations were corrected for this "blank" residue.

(b) Oxygen remaining in the apparatus after the fluorine was removed was on occasion analyzed with the mass spectrometer. Impurities amounting to less than 2% of the total were traces of N_2 and SiF_4.

3. Temperature Measurement

Two thermowells--one in the mixing chamber and one in the cryostat--were fitted with Minco No. 531-14 three-lead platinum resistance thermometers. Resistance was measured with a Leeds and Northrup G-2 Mueller bridge and Catalog No. 2430C galvanometer. The thermometers were filled with silicone oil which froze in the temperature range used. Nevertheless, the thermometers were repeatedly calibrated in liquid N_2 and LOX, and for a series of 19 calibrations conducted over a period of 3 months the standard deviation from the reference point was ±0.18°K. Temperatures other than reference points were interpolated by means of the Callendar equation and ice point calibrations.

4. Pressure Measurement

The pressures within the calibrated part of the vacuum system were recorded on a high accuracy Wallace and Tiernan pressure gage equipped with a Ni-span capsule for fluorine resistance and calibrated to ±0.1% of the total range of 0 to 225-mm Hg.

5. Stirring

O_3F_2 is much denser than LOX so that vigorous stirring was provided to prepare the saturated solution. Compartment A was therefore significantly larger than B to allow the liquid to splash freely. The stirrer plate, located close to the bottom of A, was oscillated at about 300 cycles/sec. To test the efficiency of this procedure three solubility determinations were made at 77°K with solid O_3F_2: the first solution was stirred for 1/2 hour; the second, for 3/4 hour; and the third, for 2-1/2 hours. Within the precision of measurement the results were identical. At higher temperatures O_3F_2 is liquid, and solution should be more rapid.

6. Volume Calibration

It was necessary to know the volume of both the measuring chamber and the gas analysis segments. Each was calibrated in essentially the same fashion.

The volume of a glass-stoppered glass bulb was determined by weighing the quantity of water it contained at a known temperature.

The dry bulb was connected to the solubility apparatus, the pressure of the entire system was adjusted to a preselected value, and, except for the bulb, the entire system was evacuated. The air in the bulb was then allowed to expand into the section being calibrated. The initial and final pressures were measured with the W and T pressure gage, and the volume was calculated by using the perfect gas law. The measured volumes were:

(1) glass bulb, 285 ± 1 cc;

(2) measuring compartment, 574 ± 6 cc;

(3) gas analysis loop, 2156 ± 20 and 5088 ± 50 cc.

When determining solubilities at the lower temperatures, the smaller gas loop was used. However, at 103°K the quantity of O_3F_2 dissolved required the larger loop to contain the decomposition products at a pressure within the gage range.

Variations in the laboratory temperature result in an uncertainty of the volume determinations to the extent of ±1%.

7. Analysis

Analysis of gaseous mixtures for fluorine by mercury absorption ($Hg + F_2 \rightarrow HgF_2$) is reported to be analytically satisfactory;[1] this method was used to confirm that the gases evolved arose only from O_3F_2. In the 90°K and 103°K studies the fluorine absorbed accounted for 35-38% of the total, as compared to 40% theoretical.

The gases evolved from the 77°K runs never reached pressures over 20-mm Hg; perhaps for this reason fluorine absorption by the mercury continued over periods of several days, and never attained equilibrium. Because of the apparent inadequacy of the method at the lowest temperature, all solubilities were determined solely from the total pressure of the decomposed gases.

8. Construction Details

(a) Solubility apparatus

The cryostat and the solubility apparatus were made of stainless steel. The valves were Hoke Type 440, equipped with stainless steel or Monel bellows and copper stem gaskets. The valve bonnets were welded to the cryostat lid and actuated the totally immersed valve bodies by means of heavy stainless steel extension rods. An extra bellows was welded or silver-soldered to the cryostat lid under the valve bonnet to seal the bath. A number of stainless steel guides (not shown) welded to one of the compartments on the bonnet-body line maintained proper alignment. The bath was sealed by means of a Kel-F O-ring at the junction between the lip on the flask and the lid. A series of bolts located symmetrically around the lip (also not shown) served to tighten the lid onto the lip, slightly compressing the O-ring.

(b) Vacuum flow system

The system was made of Pyrex glass and copper tubing fitted with Hoke 440 Series valves. Where necessary, stainless to copper and copper to glass Housekeeper seals or silver-soldered joints connected the flow system to the metal parts.

C. Results and Discussion

The results of the experiments are summarized in Table I. They are also presented graphically in Fig. 5, where they are compared with those of Kirshenbaum and von Grosse.

In the figure the short vertical lines are a measure of the estimated precision of each point. A major limitation of the method is the assumption of a clearcut separation of the solvent LOX from the solute O_3F_2. It is reasonable, but not certain, that the separation is quantitative within experimental error.

Table I

EXPERIMENTAL DATA

Temp. (^oK)	Mixing Time (min)	Total Gas Volume (cc)	Evolved* Pressure (mm Hg)	Residual Gas Pressure after Fluorine Absorption (mm Hg)	Dissolved O_3F_2 (g)	Wt. % O_3F_2 in LOX†
77	45	2156	13.2	**	0.052	0.0075
77	150	2156	10.9	**	0.043	0.0062
77	32	2156	8.9	**	0.035	0.0051
90	60	2156	150.3	93.0	0.60	0.092
90	71	2156	159.8	95.8	0.64	0.098
103	43	5088	124.1	82.9	1.05	0.171
103	35	5088	147.9	80.5	1.25	0.206

*Corrected for blank

**Reaction of fluorine with mercury incomplete after 24 hours

†Calculated from total gas evolved

It is tempting to point to the agreement between our result and that of Kirshenbaum and von Grosse[1] at 90°K but, by the same token, the agreement between the data at 77°K is poor. No indication is given of the method or accuracy in reference 1; therefore, it is futile to speculate on the reason for the discrepancy of the data at 77°K.

Returning to the results of this research, we note that the solubility below the melting point is below the extension of the data obtained above that temperature. This is to be expected because the solid has lower free energy than the melt.

The rather reasonable reproducibility of our results permits interpolation at intermediate temperatures. If the O_3F_2/LOX solution is ideal, the log per cent solubility versus 1/T line should be linear on either side of the melting point (for very low concentrations the weight dissolved is proportional to the mole fraction). The two points above the melting point have been used to establish the solid line in the

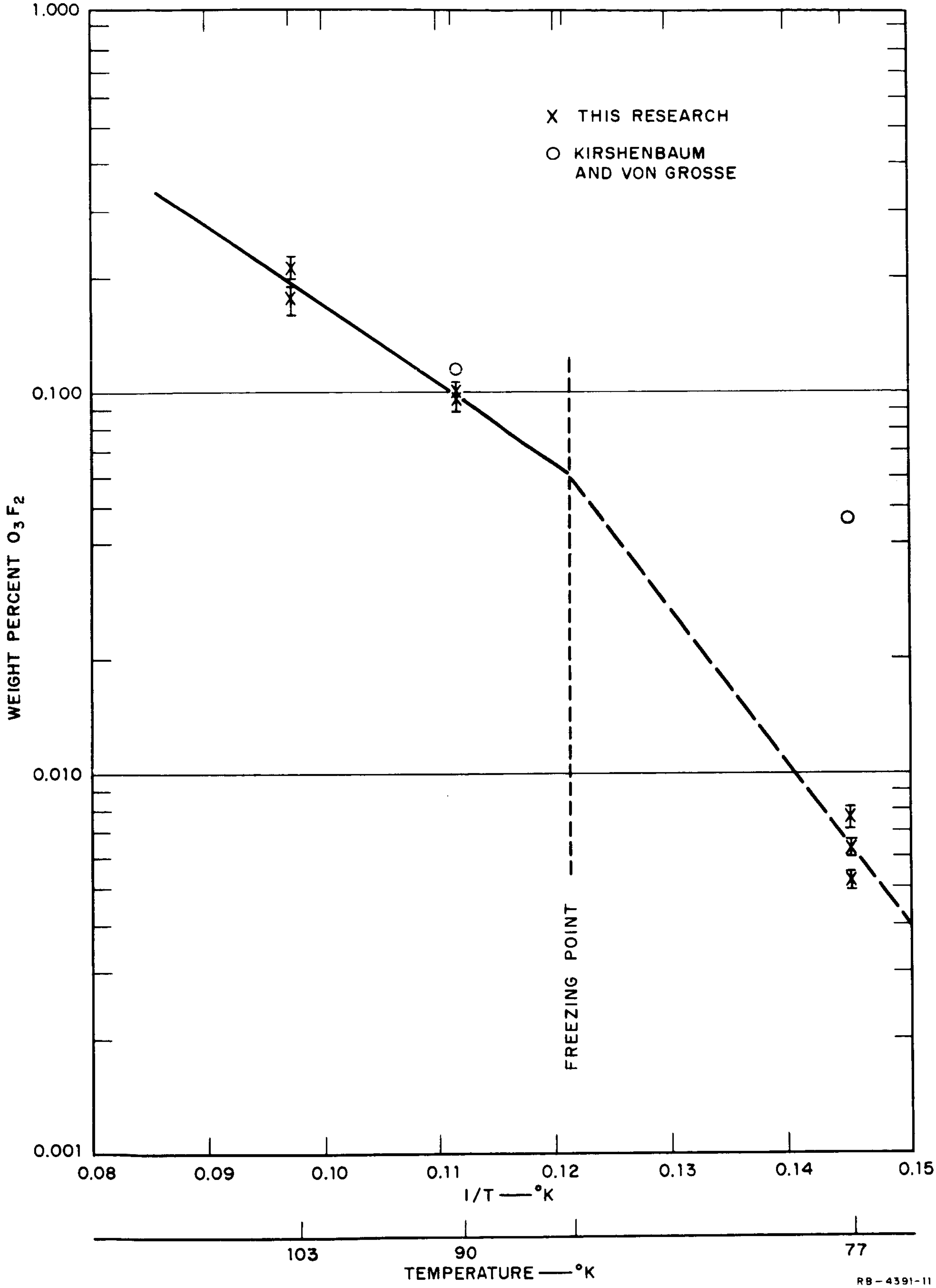

FIG. 5 SOLUBILITY OF O_3F_2 IN LIQUID OXYGEN

figure. Furthermore, the solidus and liquidus lines must intersect at the solute melting point. This is the basis for the dotted section of the solubility line.*

It is possible to proceed further along these lines and to calculate the heats of solution of the solid and of the liquid and, therefore, the heat of fusion. Admittedly the results are quite speculative but they are presented here for interest.

From the slope of the liquidus curve

$$\Delta H_{soln}^{(liq.)} = 960 \text{ cal/mole; and}$$

from the solidus curve

$$\Delta H_{soln}^{(sol)} = 5150 \text{ cal/mole.}$$

By difference

$$\Delta H_{fusion} \approx 4200 \text{ cal/mole,}$$

and therefore[1]

$$\Delta S_{fusion} = \frac{4200}{82.6} \approx 50 \text{ cal/mole/°K.}$$

(If we assume that the heats of solution may be in error by as much as a factor of two, then the range of ΔH_f is from 9820 to 580 kcal/mole; and ΔS_f ranges from 119 to 7. These results are a measure of the speculative nature of this discussion.)

The calculated value of ΔS_{fusion} is higher than values for similar materials for which $\Delta H_f/T_{mp}$ is of the order of 10-20. This suggests that O_3F_2 may be associated in the solid or that melting may introduce additional degrees of molecular freedom. Additional investigations of this point would seem in order.

*Additional measurements at a temperature between 77 K and the melting point of O_3F_2 are needed to confirm the interpolation.

V DETONABILITY OF O_3F_2

O_3F_2 is reported to have a positive heat of formation.[3] This property and the known spontaniety of its decomposition require that serious attention be given to the existence of a hazard from detonation. Reported herein are the results of experiments to establish whether O_3F_2 is detonable. The inadequacies of some methods and the successful adaptation of another to these cryogenic conditions are reported. We believe this research represents the first reliable test for low temperature detonability.

A. Discussion

To test O_3F_2 for detonability required the development of a safe method capable of distinguishing between a detonation and other explosive reactions. Detonation implies the presence of a supersonic shock wave. It follows that detonation detection should require measurement of wave velocity. However, considerable success has resulted from the assessment of explosion-caused damage and one generally used method[4] was examined for applicability at 90°K. (See below and Fig. 6 for experimental details.) Liquid oxygen was chosen as an inert sample.

In several experiments, initiation of the tetryl and propagation of the shock through the oxygen and the steel sample tube caused both the tube and the witness plate to shatter so badly as to preclude their use in distinguishing between detonating and nondetonating samples. These results were anticipated and are the consequence of the vastly changed physical properties of steel at low temperatures.

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[3] A.D. Kirshenbaum, A. von Grosse, and J.G. Aston, "The Heat of Formation of O_2F_2 and O_3F_2," J. Am. Chem. Soc. 81, 6398 (1959)

[4] "Test No. 1 - Card Gap Test for Shock Sensitivity of Liquid Monopropellants. Liquid Propellant Test Methods," Liquid Propellant Information Agency, Silver Spring, Md.

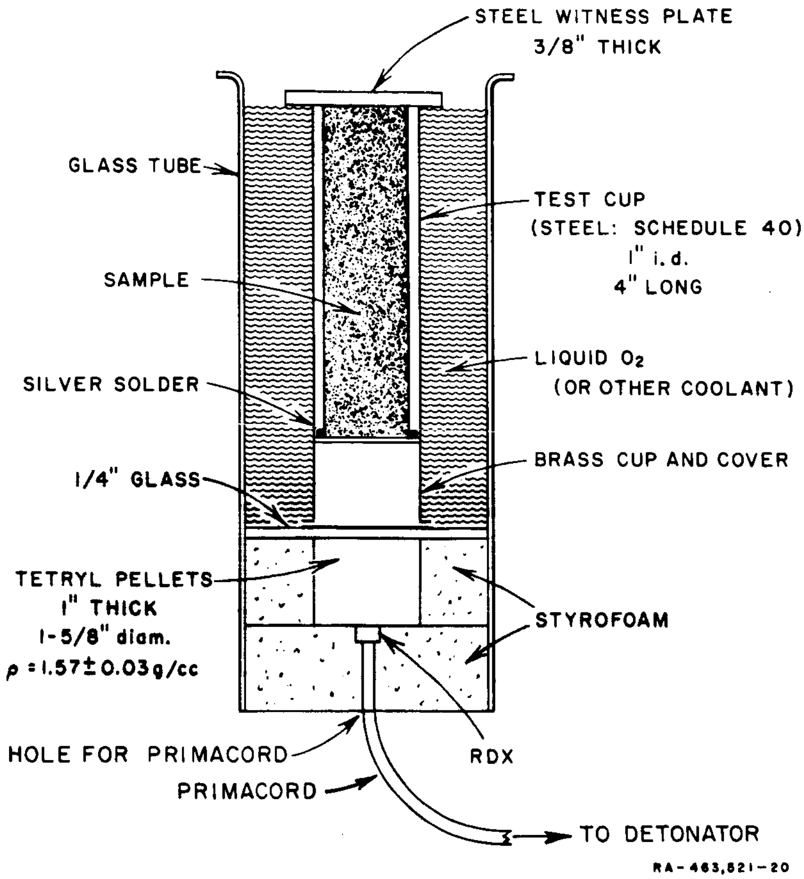

FIG. 6 DETONABILITY TEST APPARATUS

The next method attempted the measurement of shock velocity. Using essentially the same arrangement as for the previous tests, the witness plate was eliminated and a number of ionization probes were inserted, at uniformly spaced intervals, through the tube wall. At ambient temperature, this is a very reliable method for measuring shock velocities.[5] Three tests were conducted using liquid oxygen; results were nonreproducible and uninterpretable. The failure of this method can perhaps be attributed to interaction between the probes and the shock in the confinement. It is known, for example, that ionization

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[5] A.W. Campbell, M.E. Malin, T.J. Boyd, Jr., and J.A. Hull, Precision Measurement of Detonation Velocities in Liquid and Solid Explosives," Rev. Sci. Instr. 27, 567 (1956)

probes are unreliable with systems which detonate at a velocity approximating the speed of sound in the confinement.[6] A similar phenomenon may be involved here.

No additional work was done with the probes, which were replaced for detonation velocity measurements by the geometrical modification of the continuous wire[7] shown in Fig. 7. In addition, as shown, the steel cup was replaced by one of copper. The anticipated advantages were the physical independence of the wire from the confining tube and the lower speed of sound in copper versus that in steel. A set of 3 tests was conducted at 90°K: 1 with liquid oxygen, 2 with nitromethane. A typical result for each is shown in Fig. 8.[*] For liquid oxygen, when the tetryl at the liquid interface detonates, the voltage across the wire drops slightly from the zener potential but rises rapidly to the original limiting value, a result roughly typical of inert substances. With solid nitromethane, after an initial transition period, the voltage drops linearly with time for a period corresponding to that during which the nitromethane is detonating stably. This is typical of stably detonating materials, and the detonation velocity can be calculated directly from the value of dE/dt along this linear portion. For details the reader is referred to Reference 5.

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[6] A. B. Amster, R. L. Beauregard, G. J. Bryan, and E. K. Lawrence, "Detonability of Solid Propellants I. Test Methods and Instrumentation," Navord Report 5788, U. S. Naval Ordnance Lab., White Oak, Md., 3 February 1958

[7] A. B. Amster, P. A. Kendall, L. J. Veillette, and B. Harrell, "Continuous Oscillographic Method for Measuring the Velocity and Conductivity of Stable and Transient Shocks in Solid Cast Explosives," Rev. Sci. Instr. 31, 188 (1960)

[*] Here and in Fig. 9, the illustrations are of tracings; the originals were unsuitable for reproduction.

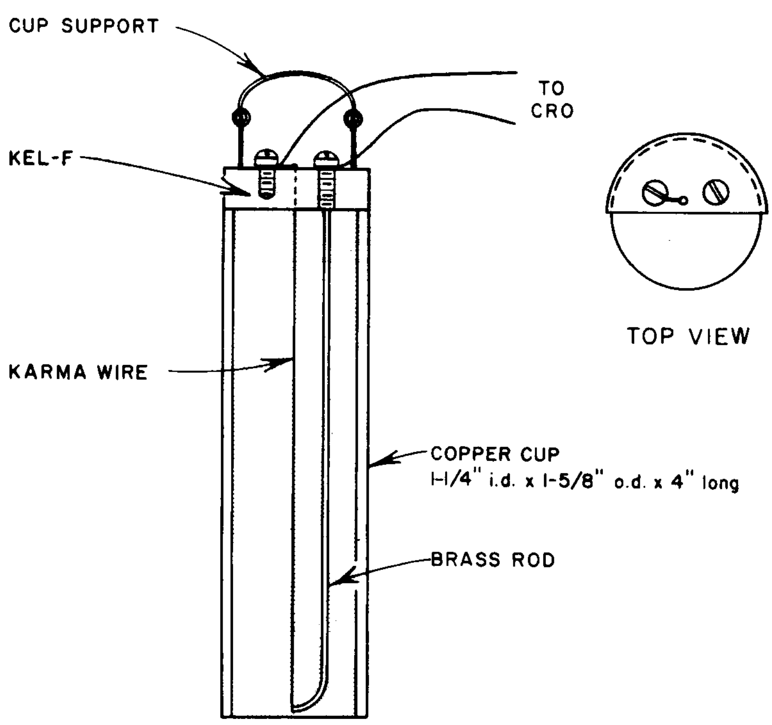
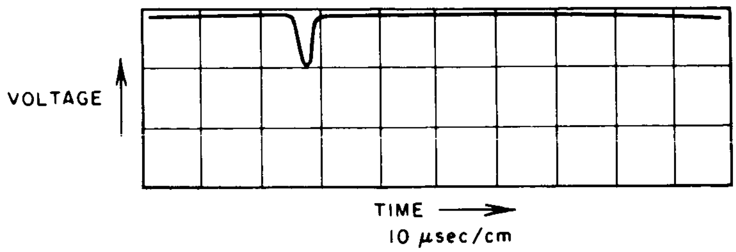
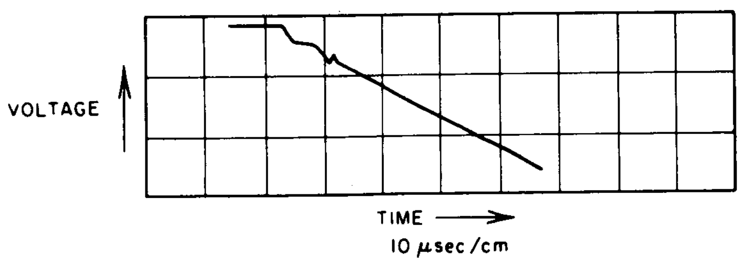


FIG. 7 MODIFICATION OF TEST CUP



(a) INERT ACCEPTOR: LIQUID OXYGEN



(b) DETONABLE ACCEPTOR: NITROMETHANE

RA-463,521-22

FIG. 8 TYPICAL DETONABILITY TEST RESULTS

Having established that the wire method is as reliable at 90 °K as at ambient temperature, two tests were conducted with O_3F_2. A typical oscillograph, Fig. 9, shows the potential drop starting at that for the entire wire in the closed circuit. When the shock wave reaches the interface, there is slight evidence of ionization, but within ~ 3 μsec, the potential returns to the limiting zener value.*

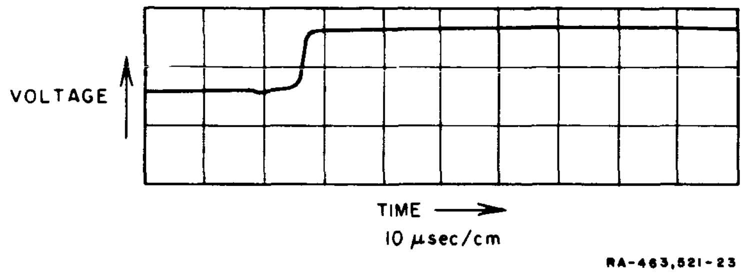


FIG. 9 O_3F_2 DETONABILITY TEST

B. Experimental

Among the dimensions and other experimental parameters not shown in Figs. 6 or 7, the following are pertinent. The bottom of the test cup is 0.005-inch-thick brass sheet silver-soldered to the steel. The top of the brass cup is fabricated in similar fashion. Thus, 0.01 inch of brass separates the tetryl donor from the sample. The glass partition is approximately 1/8 inch thick; this dimension is not critical. After insertion of the tetryl pellets the cover is sealed to the brass cup

*If the resistance wire is initially insulated from the brass rod (Fig. 7) the starting voltage is determined by the limiting zener potential, and records like that of Fig. 8a are obtained. When the wire makes contact with the rod the starting voltage is determined by that across the wire, and records like those of Figs. 8b and 9 result. For the present research it was convenient to cement the wire to the rod when testing liquid oxygen; for safety cement was not used and a firm metal contact was employed in the nitromethane and O_3F_2 tests. It is only this difference in the electrical circuit which accounts in particular for the difference between Figs. 8a and 9.

by means of a thin ring of fluorocarbon grease spread on the cup lip. This effectively precludes contact of the coolant with the tetryl.

Initiation is accomplished with an exploding bridgewire (EBW) detonator followed by 18 inches of Primacord. Unless the Primacord is used, the electrical disturbance caused by the EBW will obscure the desired data. The electrical leads from the sensing wire to the power supply, ordinarily of coaxial cable, are of rubber-insulated stranded AWG 14 copper wire ("lamp cord") and are quite satisfactory. The sensor wire is potentiometer grade KARMA, 349.5 Ω/ft.

Although the general principles of shock testing and of using the continuous wire have been explained quite adequately elsewhere, it is pertinent to discuss the reasons for the geometry employed here. Largely a result of safety requirements, the design affords assurance to the experimenter that he is exposed to no risk greater than that normally encountered with the use of well-known, reliably safe, explosives. As preparation for these experiments, it was established that even powdered tetryl (more sensitive than pellets) and liquid oxygen are compatible; nevertheless, the tetryl pellets in the experiment were protected from oxygen by the brass cup and glass septum. The latter permits insertion (or removal) of the detonator-RDX initiator either before or after coolant is added to the upper chamber. To prevent unnecessary warming of the sample when testing the O_3F_2, the tubes were filled elsewhere, were suspended via the wire and supports shown in Fig. 8, and were transferred and lowered (by remote control) into the test cell. A metal guide within the test cell (not shown) served to keep the tetryl cup centered and to guide the sample into line above the cup. The use of specially designed Dewar flasks to reduce oxygen consumption would increase the net cost.

C. Conclusions

Conventional damage criteria were found valueless in discriminating between a detonation and an explosion in energetic materials at 90°K. So, too, were ionization probes inserted through the walls confining the sample. By a simple geometrical modification the continuous wire technique has been shown to be valuable and has been used to confirm that O_3F_2 is nondetonable in the diameter tested.

VI STORABILITY OF O_3F_2 AND O_3F_2-LOX SOLUTIONS; COMPATIBILITY WITH ROCKET CONSTRUCTION MATERIALS

A. Neat O_3F_2 Storability and Compatibility Trials

Ten different materials commonly used in rocket engine hardware were studied in these trials. Duplicate, polished, LOX cleaned, dried, and weighed samples of each material were stored in sealed glass tubes with neat O_3F_2. Fire-polished samples of glass were used as controls.

Each sample, a 1/4-inch-diameter x 3/8-inch-long rod, was placed in a glass tube, approximately 5/16-inch i.d. x 5-inch-long, and prechilled with LOX. Sufficient neat O_3F_2 was added to cover the sample, and the open end of the tube was sealed quickly with an oxygen torch. To prevent decomposition of the O_3F_2, the lower end of the tube was cooled to 77°K (LN_2 bath) during sealing.

Because O_3F_2 decomposes at 77°K in light and the sealing operation involved exposure to considerable sodium vapor light, the samples were reexamined at 90°K in a LOX bath. The samples, found to be molten and free flowing in the LOX bath, were stored in LOX.

After 24 hours at 90°K in total darkness, the samples were examined again and were found to contain a significant quantity of solid product. After three days the amount of liquid remaining was negligible. A solid product, orange in color (probably O_3F_2), remained in the tube.

After 2 weeks the sample tubes were crushed, and the orange solid was decomposed by warming to room temperature in an inert atmosphere dry box ($O_2F_2 \rightarrow O_2 + F_2$). The original and final weights of the specimens are listed in Table II.

The weight changes appear to be insignificant and normal for reaction with fluorine. All the samples except stainless steel, Kel-F, and glass (which had become slightly pitted) had lost their original luster and were coated with a dull deposit. All the storage tubes showed evidence of etching.

Table II

EFFECT OF O_3F_2 UPON WEIGHT OF STORED SAMPLES

Sample		Final Weight (g)	Weight Change (g)
Mild Steel	1	2.3416	+0.0008
	2	2.3390	+0.0009
Cu	1	2.6627	+0.0006
	2	2.6628	+0.0014
Ni	1	2.7332	+0.0019
	2	2.7501	+0.0009
Monel	1	2.7334	+0.0010
	2	2.7372	+0.0012
Steel 4340	1	2.4175	+0.0012
	2	2.4119	+0.0013
Al 2024	1	0.8608	+0.0011
	2	0.8522	+0.0004
Al 6061	1	0.8388	+0.0005
	2	0.8407	+0.0024
Brass	1	2.5742	+0.0013
(Red Comm)	2	2.5857	+0.0012
Kel-F	1	0.6656	+0.0001
	2	0.6578	0.0000
SS304	1	2.4201	-0.0001
	2	2.4196	+0.0001

To compare storability of O_3F_2 at 77° and 90°K, duplicate samples of both copper and glass were prepared as outlined above. One sample of each was stored at 77°K; and one, at 90°K. The samples stored at 77°K (LN_2bath) were removed from storage frequently, melted momentarily in LOX to check for evidence of decomposition. After the first 2 or 3 months of storage, depending upon the material, decomposition of O_3F_2 on the tube walls was noted; after 6 months in storage, approximately three-fourths of the stored O_3F_2 had decomposed.

Samples stored as a liquid at 90°K were decomposed completely after three days.

B. Storability of O_3F_2 - LOX Solutions

O_3F_2 is soluble in LOX to about 0.095% at 90°K and to about 0.007% at 77°K. Duplicate samples of both copper and glass were prepared as noted above and were covered with about 5 cc of LOX saturated with O_3F_2 at 90°K. One sample of each was stored at 77°K; and one, at 90°K. The samples stored at 77°K had not completely lost the characteristic pale yellow color of a freshly prepared solution even after 6 months' storage, whereas samples stored at 90°K lost this characteristic color after approximately 1 month.

VII ROCKET MOTOR IGNITION STUDIES

A. Experimental Flow Facility

The ignition processes for the propellant system LH_2 and LOX/O_3F_2 were studied by using a small combustion chamber incorporating either single or multielement injectors.

In support of a previous program, a conventional LOX/LH_2 pressurized-feed flow system had been assembled for studies on LOX and LH_2 + metallic fuel tripropellants. The system was designed for relatively high flow rates and used a combination of simple vacuum-jacketed and Pearlite-insulated lines. (By present day standards these are grossly inefficient.) The flow system was comparable with many others and has performed well where a long chill-down cycle prior to ignition is acceptable, and where flow rates during combustion are sustained at a high level.

The current study of ignition processes required very small flow rates on an intermittent basis. The heat insulation in the lines was inadequate and caused wide variations in line temperature and excessive consumption of LOX during sequential chilling operations (up to 10 replicate experiments during a day). The large volume of liquid oxygen needed to chill the chamber condensed atmospheric moisture, and the condensate interfered with the resolution obtainable from the high speed camera.

To overcome these problems, an internal liquid nitrogen chill line was tried; though this enabled some tests to be performed, it was not uniformly successful. Data obtained from the first trials clearly demonstrated that insulation needed to be improved significantly if O_3F_2 were not to decompose between the LOX tank and the ignition test chambers.

Alternate flow lines were studied, and the decision was made to use either superinsulated vacuum lines or liquid-jacketed lines for the LOX/O_3F_2; the system was also improved by installing a superinsulated vacuum line for the liquid hydrogen feed to the ignition test chamber. The system installed for the final trials gave the expected advantages in the operation of the flow system.

To increase the precision of the on-off control of propellant flow the massive electro-pneumatic valves originally installed were discarded in favor of expendable lightweight solenoid valves. The valves selected, with one exception, operated satisfactorily when fully immersed in liquid nitrogen.

B. Experimental Approach

A number of unusual problems arose in the study of the hypergolic characteristics of LOX/O_3F_2 solutions with liquid and gaseous hydrogen. These included:

(1) the rapid decomposition of O_3F_2 at temperatures above 110°K

(2) the attainment of hypergolicity only in the presence of the liquid phase solution

(3) the hypergolicity of LOX/O_3F_2 with most organic materials

(4) the requirements of extremely low flow rates for single-element injectors necessitate extremely good thermal insulation of the system

(5) the complexity of photographic and instrumentation procedures at extremely low temperatures.

With these difficulties in mind, two types of ignition test chambers were designed. The first was a double-walled transparent chamber (Fig. 10) fabricated from Vycor (quartz) and fitted with a single element injector. This was used for optical studies at pressures below 100 psi. A steel ignition test chamber was also fabricated for studies involving multielement injectors at pressures up to 500 psi (Fig. 12). The combination of the two types of studies was considered desirable in order to correlate observed physical phenomena with observations made with normal instrumentation.

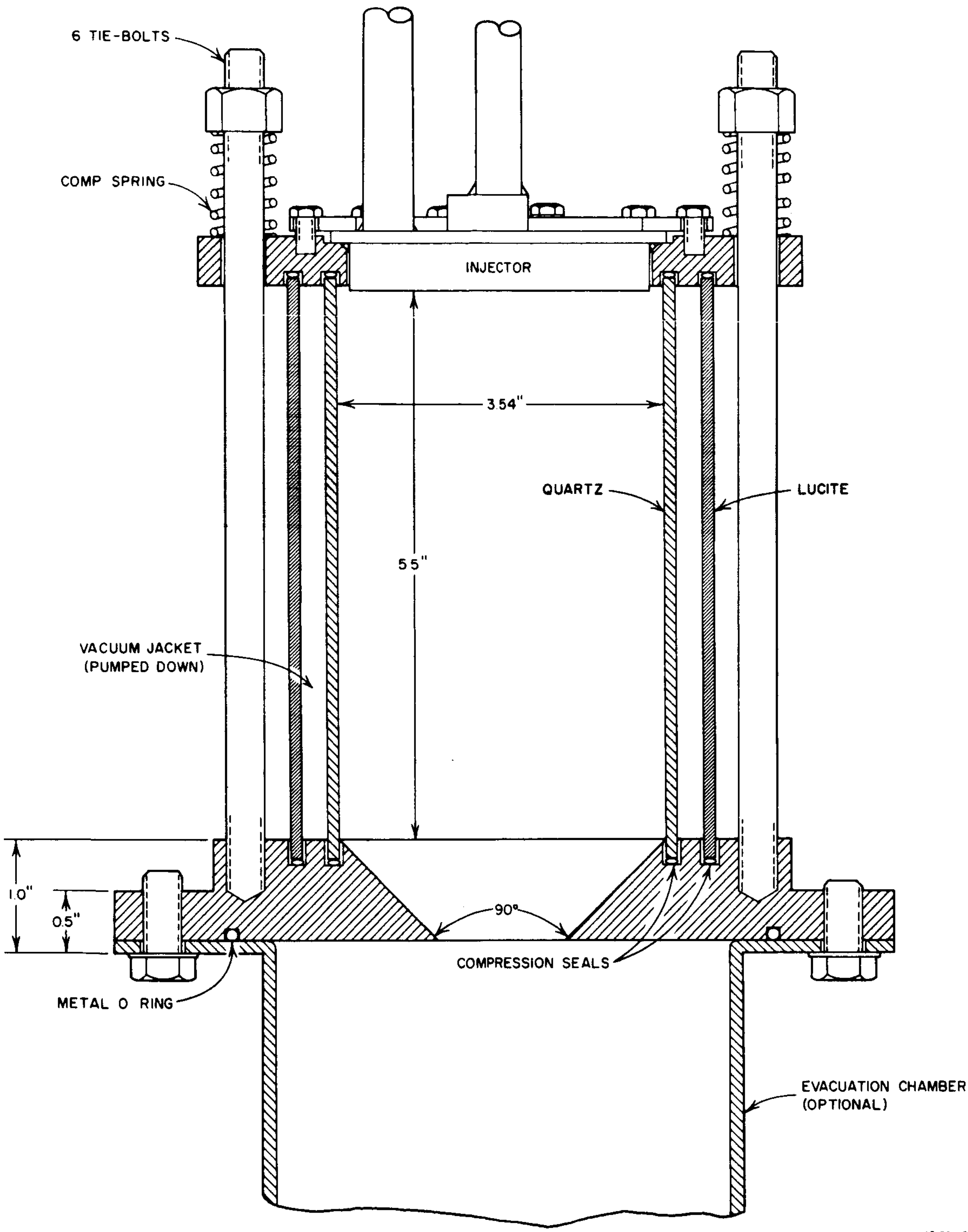


FIG. 10 QUARTZ IGNITION CHAMBER (fabricated from either quartz or Vycor)

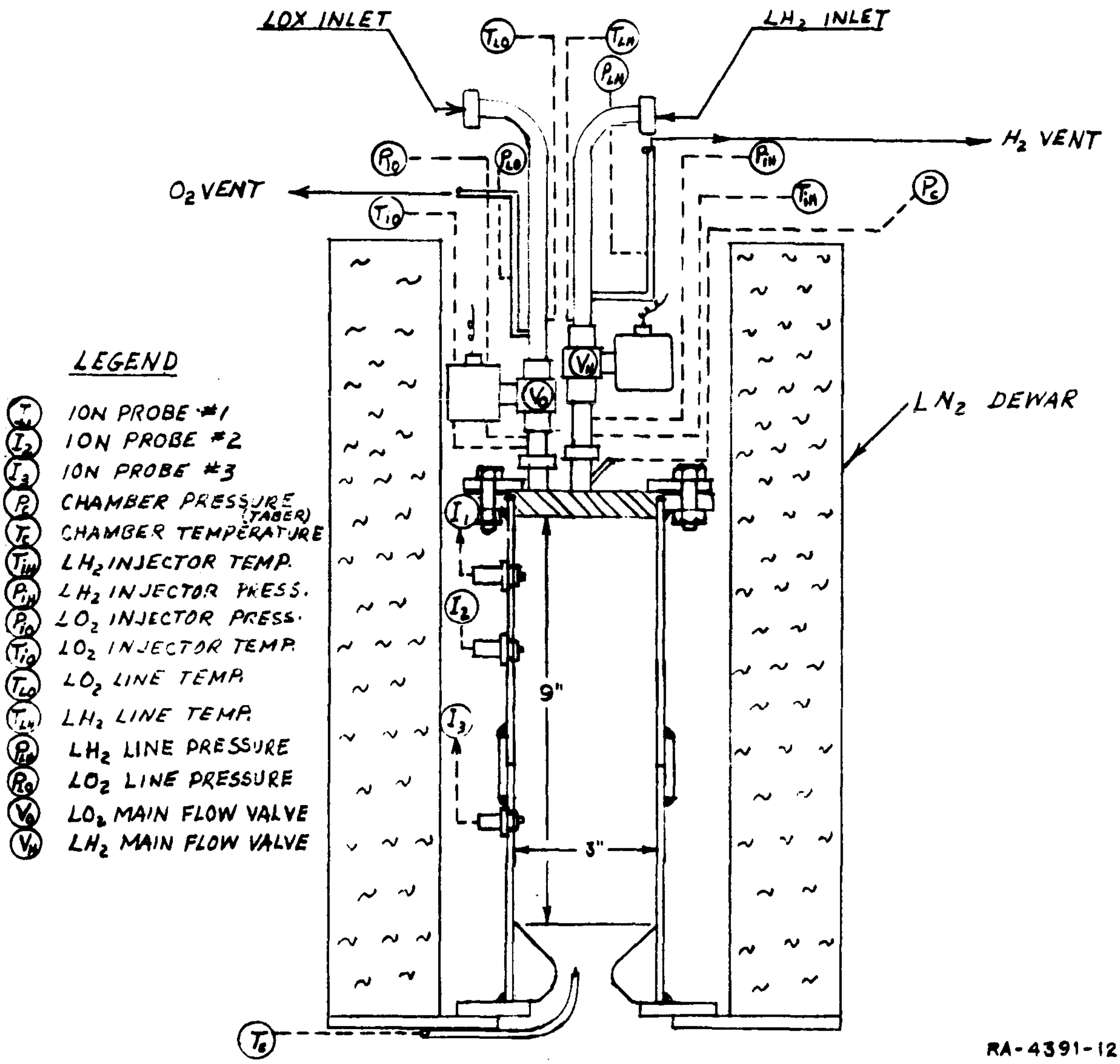


FIG. 11 STEEL COMBUSTION CHAMBER ASSEMBLY SHOWING INSTRUMENTATION TRANSDUCERS

Two principal types of injector have been selected for continuous study with LOX/O_3F_2, the coaxial stream injector and the triplet injector. Cold flow tests of the single element triplet injector are shown in Fig. 13, while the flow tests on the multielement coaxial stream injector (LOX core) are shown in Fig. 14. The injector element configuration used in these trials of both types of coaxial stream injectors, liquid oxygen core with a hydrogen annulus, was selected to duplicate that used in many aerospace LH_2/LOX engines.

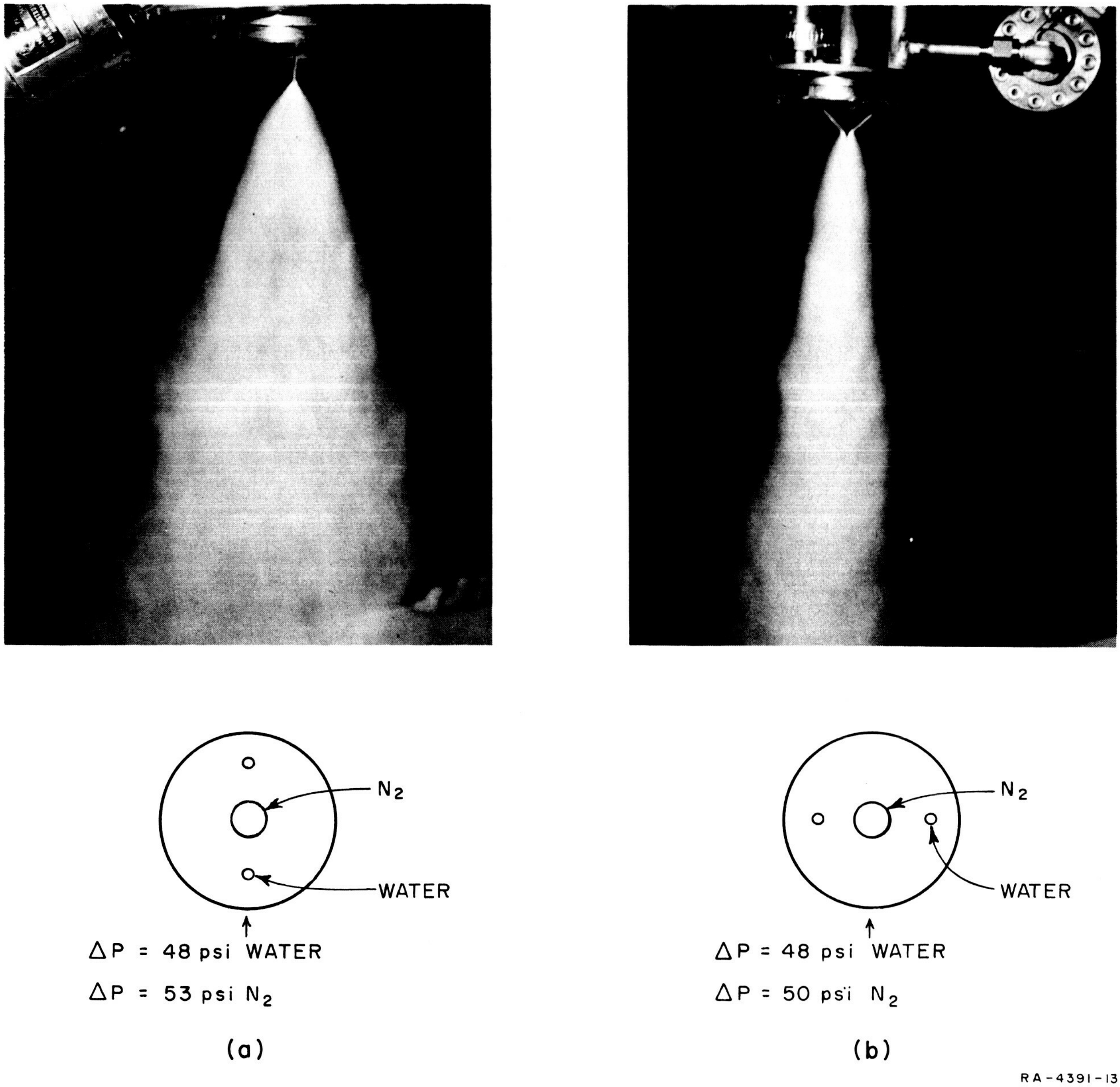


FIG. 12 FLOW TEST OF SINGLE ELEMENT TRIPLET INJECTOR.
GASEOUS NITROGEN IN CENTER, WATER IN OUTER JETS.

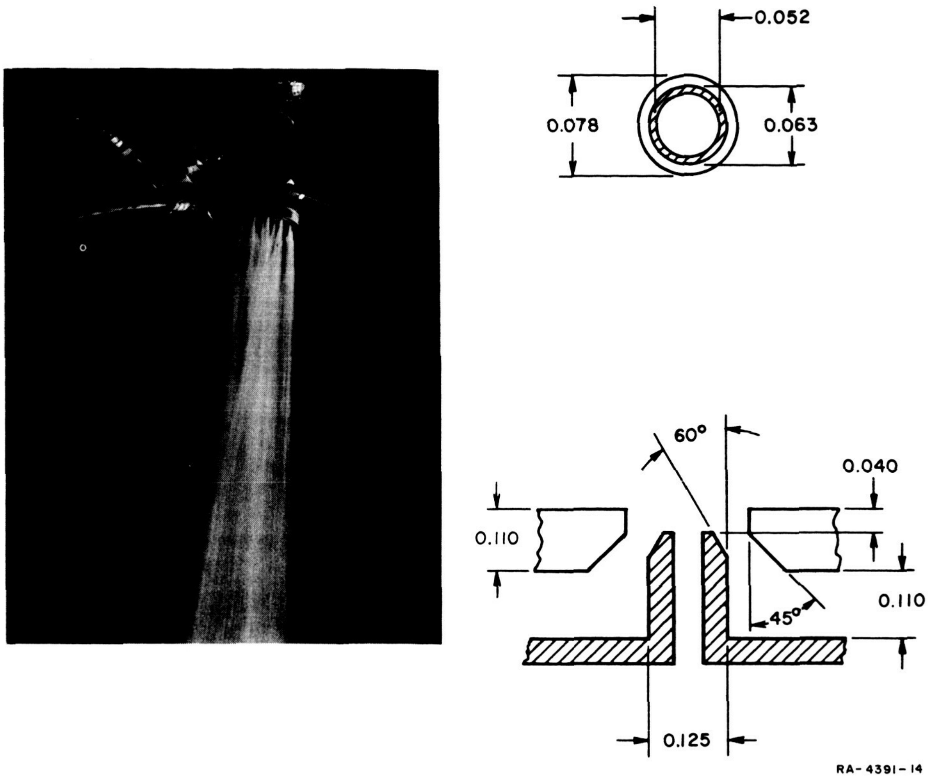


FIG. 13 FLOW TEST OF MULTIELEMENT COAXIAL STREAM INJECTOR. GASEOUS NITROGEN IN ANNULII, WATER IN CORES — INCLUDING SINGLE ELEMENT GEOMETRY

C. Ignition Tests

In the first test series a single element triplet injector was used in the Vycor motor chamber shown in Fig. 10. The nominal thrust of this engine was 100 lbs. Cameras were used with the quartz chamber to give convincing correlation with the photo cells, pressure gage, and thermocouple instrumentation. The aim of the tests was to measure the ignition delay with O_3F_2-saturated LOX and cold gaseous hydrogen. The hydrogen gas was cooled by passage through a coil submerged in liquid nitrogen.

The test summary for this series is in Table III; the erratic results are partially attributed to the questionable physical state of LOX reaching the injector. Data analysis confirms that when the LOX/O_3F_2 temperature is above 120°K, significant decomposition of O_3F_2 takes place, and ignition does not occur. The long ignition delays were associated with gaseous or intermittant gas-liquid flow in the oxidant lines. The movie film taken during these tests confirmed that ignition occurred immediately after liquid appeared at the injector. It was concluded that the delay data from this test series were biased by intermittent gaseous oxygen flow caused by heat leakage into the lines under minimal flow conditions.

A single element coaxial injector with gaseous hydrogen flowing through the outside annulus was tested in the transparent combustion chamber. Three separate tests gave photographic evidence that ignition occurred 49 milliseconds after liquid oxygen started to flow. It was apparent that premature vaporization and decomposition of O_3F_2 invalidated this test series. Following this test series the major modifications previously referred to were made, the oxygen line was replaced with a LOX-jacketed line and a Linde superinsulated line was installed on the hydrogen side.

The improved flow system was tried out in a series of experiments using liquid hydrogen and liquid oxygen. The tests were carried out in a stainless steel chamber with a 20-element coaxial stream injector. The data are summarized in Table IV. The experimental setup is shown in Fig. 14, and it should be noted that the solenoid-operated main flow valves were also immersed in liquid nitrogen as indicated in Fig. 15. For this series the contraction ratio of the chamber was 5.9, the L^* was 58, and the length was 9 inches.

Ignition was detected by using multistation ionization gages in the chamber and one gage outside to detect "blow-back" ignition. Two such "hard-starts" (Runs 43 and 47) occurred under conditions where appreciable quantities of hydrogen flowed prior to LOX delivery. This condition came about because of sluggish operation of the LOX main flow valve. (After the experimental program was completed, this valve was cut apart. A metal plug had blocked the flow from the bleed hole which empties the liquid from behind the actuator rod. This was not found on valves ordered prior to or after this one was procured.)

In Run 38 an ignition delay time of 11 milliseconds is reported. Although the LOX tank valve failed to open and only the LOX line pressure was available to push LOX through the injector, this was sufficient to cause ignition.

Table III

MEASURED IGNITION DELAYS FOR TRIPLET INJECTOR AND GASEOUS HYDROGEN

Test No.	LOX Lead Time, m secs.	Ignition Delay, m secs After H_2 Pressure at Injector: Based on P_c	Based on T_c	Photo-cells	Based on Movie Film	$\dot{\omega}$, (lb/sec)	O/F	Peak P_c,* PSIG	LOX Injector Temp. during Flow, (°K)	Hydrogen Injector Temp. during Flow, (°K)
23	130	17	20	20	19	0.123	10.6	62	74	225
24	120	Programming System Breakdown								
25	120		No Ignition			---	--	---	150	238
26	120		No Ignition			---	--	---	148	239
27	120	800	---	800	N.A.**	0.127	8.3	105	138	204
28	120	108	---	108	N.A.	---	--	47	115	205
29	120	87	89	88	23	0.123	10.6	69	115	221
30	120	9	9	9	10	0.125	8.7	74	112	218
31	120	67	67	67	18	0.128	8.1	53	120	221

* Not nozzled for this flow rate

** Not assessable

Table IV

MEASURED IGNITION DELAYS FOR 20-ELEMENT COAXIAL INJECTOR WITH LIQUID HYDROGEN

Test No.	LOX Lead Time, m secs.	Ignition Delay, m secs After H_2 Pressure at Injector		$\dot{\omega}$ (lb/sec)	O/F	Steady State P_c, PSIG	LOX Injector Temp. during Flow (^oK)	Hydrogen Injector Temp. during Flow (^oK)
		Based on P_c	Based on Ion Gage					
37	91	1	2	.693	8.68	140	77	32
38	94	---	11	*	*	---	--	52
39†	55	---	8	**	**	---	77	73
40††	55	---	11	**	**	---	77	73
41†	14	40	40	.727	11.33	140	77	35
42††	14	4	4	.790	13.22	102	77	77
43	12	110ϕ	110	.749	9.72	145	77	23
44†	31	34	34	.804	10.44	110	77	60
45††	31	40	40	.785	12.29	120	77	72
46†	31	5	5	.628	11.18	110	77	46
47††	31	95ϕ	95	.659	11.78	110	77	55
48†	64	10	10	.585	9.63	93	77	53
49††	64	25	24	.541	7.86	93	77	57

* LOX tank valve closed
** P_c amplifier drifted
ϕ Blow-back ignition
†-†† Denotes consecutive runs with less than 60 sec. between firing

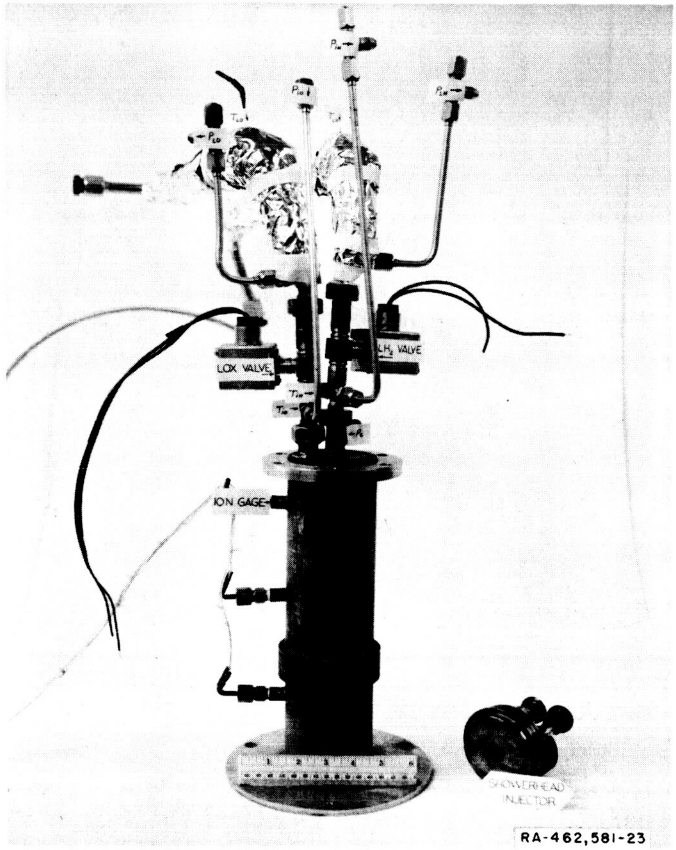


FIG. 14 COMBUSTION CHAMBER PRIOR TO INSTALLATION IN LN_2-JACKET

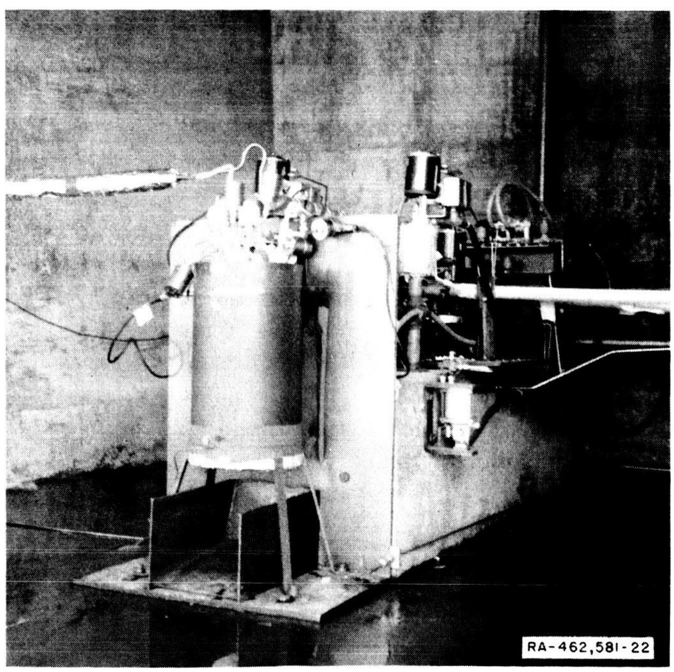


FIG. 15 TEST STAND INSTALLATION SHOWING LN_2-JACKETED COMBUSTION CHAMBER

In this test series the ignition delay did not appear to be a function of the LOX lead time. If the hard starts are discarded, all delays were rather randomly distributed below 40 milliseconds. Even though LOX lead times were varied from 14 to 94 milliseconds, ignition delays of 10 milliseconds or below were measured through the lead time range. Under the conditions of these experiments, it is concluded that ignition occurs as soon as liquid oxygen with O_3F_2 contacts hydrogen and that the scatter in experimental measurements is due primarily to minor fluctuations in the characteristics of LOX flow between the flow control valve and the injector face. Flow system characteristics and operation procedures caused the flow fluctuations. For instance, if a consecutive run was made with less than 60 seconds between firings, both oxygen and hydrogen were nearly always hotter in the flow lines than when these lines were prechilled before firing. It was also apparent that the flow fluctuations in LOX delivery were caused by the sluggish and unpredictable operation of the LOX valve rather than by the control introduced by adjustment of the LOX flow lead time. Regardless of these operation difficulties, which are peculiar to operating an experimental engine with O_3F_2, it appears that all ignition delays are within a usable range and the potential for delays under 10 milliseconds is excellent. One significant result was confirmation of a clear correlation between ignition failure and the presence of gaseous oxygen at the injector. A plot of LOX line temperature for the ignition tests on the saturated pressure versus temperature relationship for liquid oxygen shows that successful ignitions are shaded to the liquid side of the line, and failures are shaded to the gas phase side of the line (Fig. 16).

D. Ozone Fluoride Field Transfer

For a given test series ozone fluoride in excess of that required to saturate a full LOX storage tank for the engine was made in the laboratory and was transported frozen in liquid nitrogen to the static test site. Prior to being added to the mix tank (Fig. 17), the O_3F_2 in the 50-ml glass flask was melted in liquid oxygen. Meanwhile the mix tank was topped with LOX and transfer operations were begun. The

O_3F_2 was poured rapidly from the flask into the LOX-cooled funnel and drained into the tank. The contents were agitated for 20 minutes with an air-operated paddle agitator and then were transferred to the LOX storage tank.

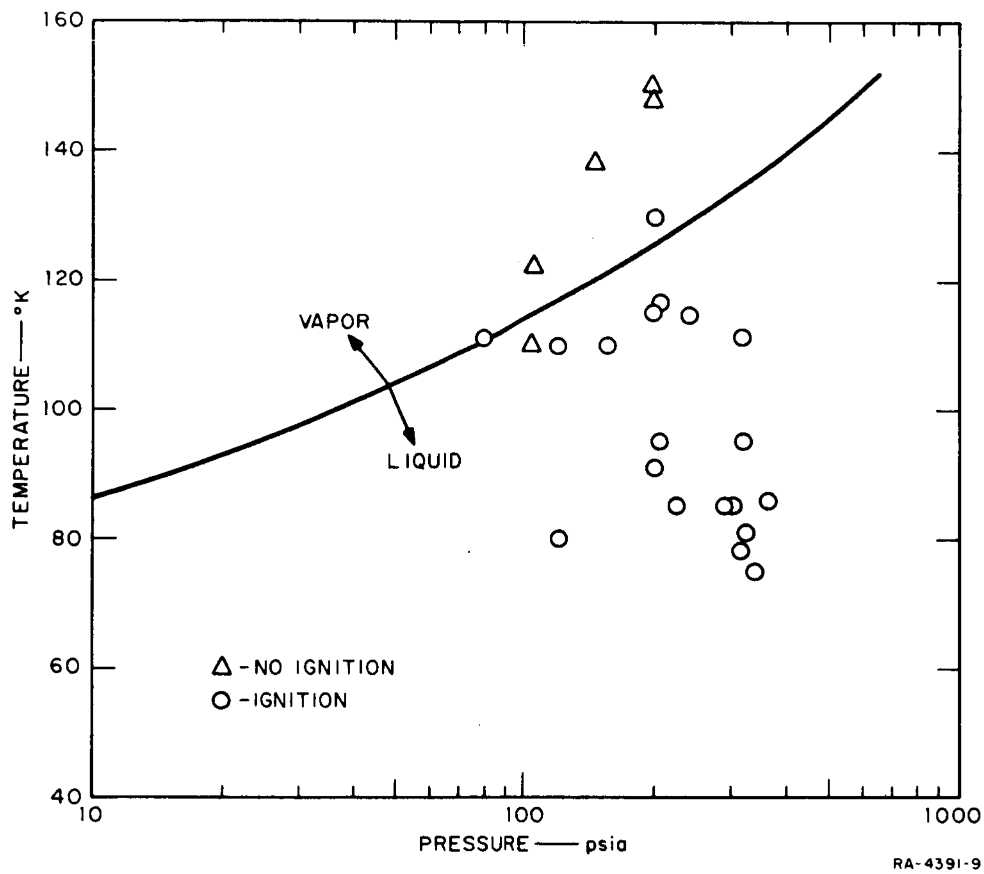


FIG. 16 PLOT OF EXPERIMENTAL FIRING DATA

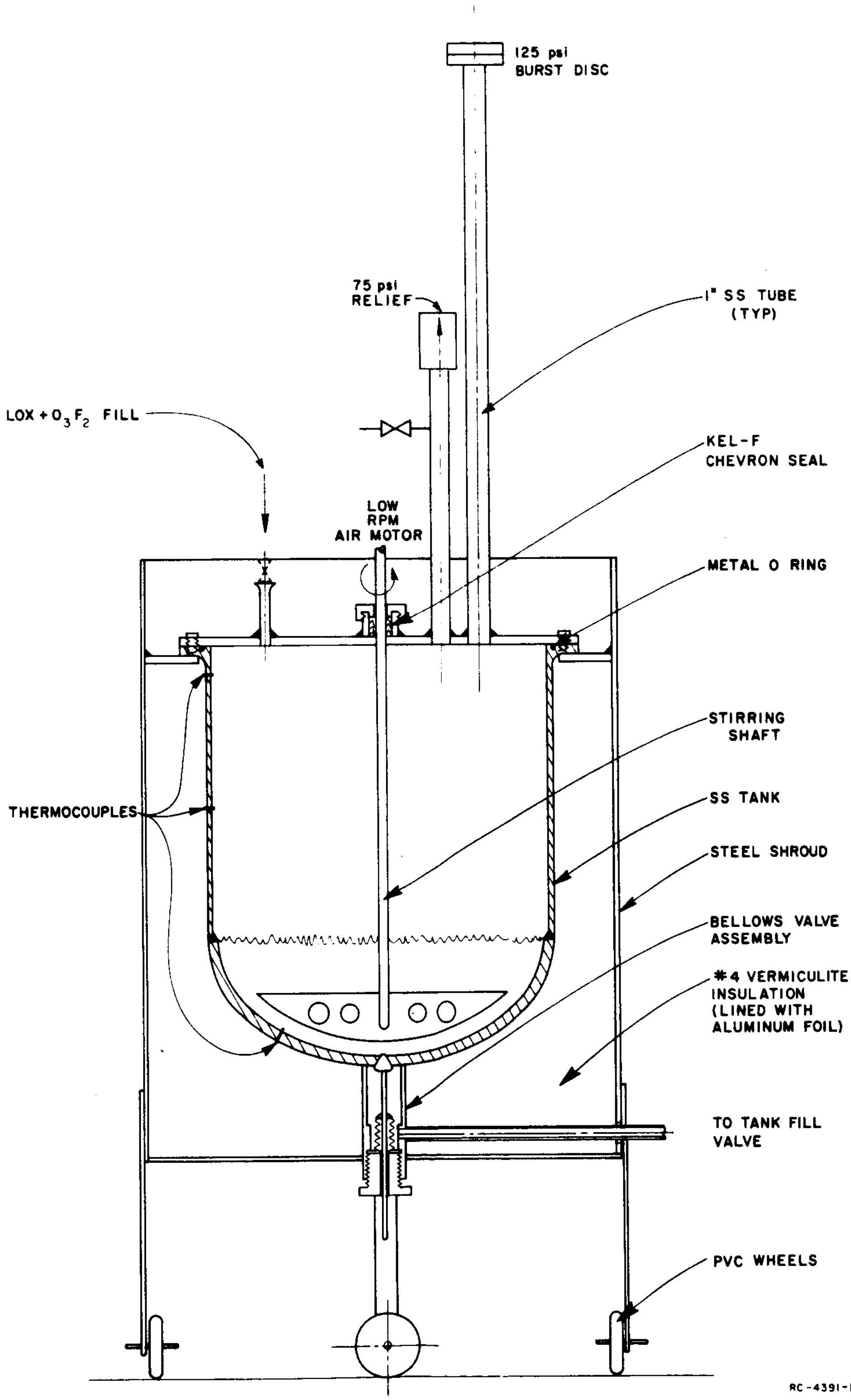


FIG. 17 MIX TANK FOR O_3F_2 (schematic)

E. Instrumentation and Data Reduction

1. General

Measuring of the transient flow and combustion parameters in the small ignition test engine gave rise to many problems, and other problems arose because of the corrosive nature of O_3F_2. The hypergolicity of LOX/O_3F_2 precluded easy recalibration or replacement of transducers once a test series was begun. Parameters to be measured included pressures, flow rates, bulk liquid temperature, injector and chamber temperature, light emission, and ionization.

In the early stages of the study it had been hoped to use close-coupled, fast response, piezo-electric gages, but the drift associated with transient temperature gradients rendered their use impractical. Accordingly, medium-response Taber pressure transducers were selected; these were coupled through a short length of stainless steel pipe to help reduce the temperature gradient effects. In most trials the inclusion in the line of relatively warm gas prevented cryogenic fluid from affecting the accuracy of the calibrations. O_3F_2 corroded the transducer diaphragms, and these had to be replaced after each test series.

Temperature measurement was carried out using gold/cobalt versus copper thermocouples in conjunction with a liquid nitrogen reference junction. The couples were soft soldered together; they were inserted into the lines by using ceramic insulated seals. The problem of heat leakage biasing the junction temperature was minimized by using thin wires and by placing the junction as far into the stream as possible, consistent with structural rigidity of the probe.

2. Ignition

Chamber thermocouple and ionization gages were used to detect ignition. While thermocouples in most instances burned out, the ionization gages were found to be sturdy and did not break down during use. With the quartz chamber, solid state, uv-sensitive photo cells were satisfactory.

Measurement of propellant flow rate was needed, and it was hoped to use turbine flow meters for this purpose. During preliminary trials a turbine flow meter was found to perform reliably only on an intermittent basis; when it was used with LOX/O_3F_2, corrosion was observed and it did not function satisfactorily. Flow measurements were consequently made by determining the pressure drop across the injector or valve control orifices, flow calibration being carried out using water and a precision flow meter. Appropriate corrections were made for the different fluid characteristics of water and the propellants.

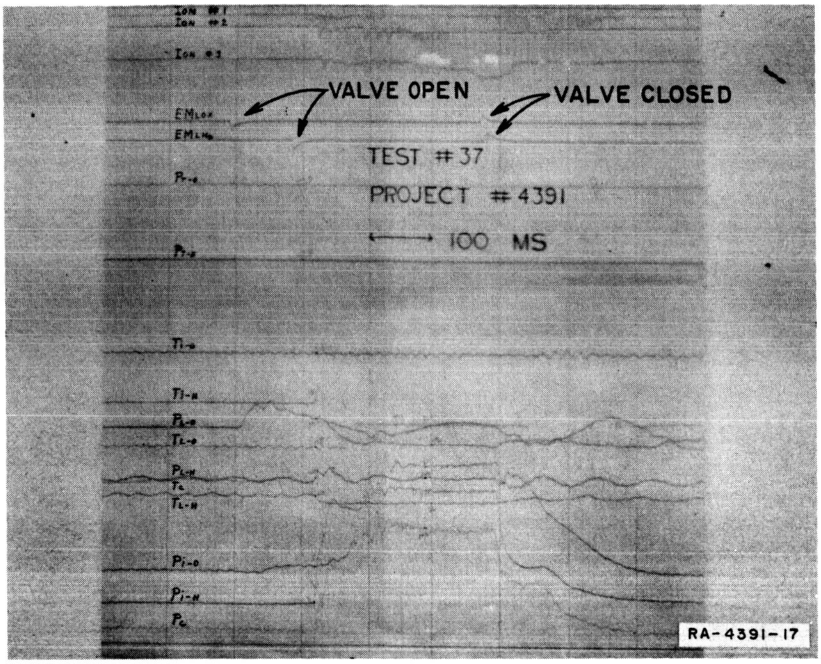
3. Data Acquisition

Data from the various transducers were recorded by means of a 35-channel Visicorder with a 7-channel, high speed tape recorder as back-up for critical data channels.

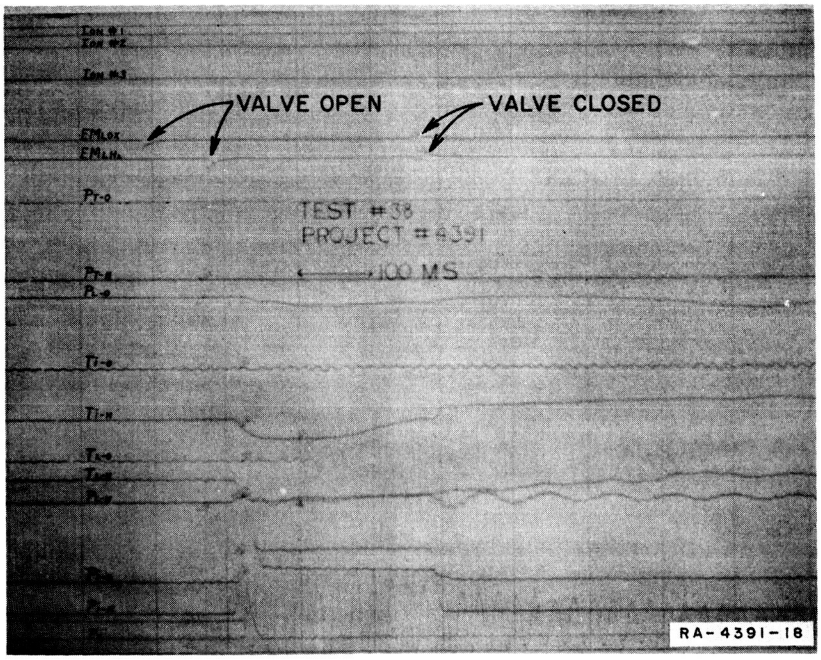
Before each test series, calibration steps were recorded, and for each run, base level outputs of the transducers were verified. Chill-down and venting sequences were carried out until the line thermocouple registered the appropriate temperature. On closing of the vent lines, the automatic sequencer programmed the opening and closing of the propellant flow control valves. For the final tests the combustion chamber was automatically purged (last test series only).

Typical test data for the multielement coaxial stream injector are shown in Fig. 18 (a) and (b); the locations of the transducers are given in Fig. 11.

Ignition measurements made from instant of pressure rise, light emission, ionization transient, high speed movie film, and chamber temperature rise; all results correlated well with one another. The major measurement problem was determination of the instant of delivery of fuel and oxidant to the injector; injector pressure rises were considered the best guide when visual analysis of the injection processes was precluded.



(a)



(b)

FIG. 18 FIRING RECORDS FOR MULTIELEMENT COAXIAL STREAM INJECTOR

F. Discussion of Results from Ignition Studies

These initial experiments carried out on the ignition of hydrogen by LOX/O_3F_2 have shown that with the triplet injector configuration, hypergolic ignition occurs within 20 milliseconds of the bringing together of the fuel and oxidant streams. The ignition was observed to occur at the point of jet impingement.

The coaxial stream injector of the type used in typical rocket engines was studied under a carefully controlled environment. For reasons believed to be connected with injector face cooling, the injector flow pattern has normally been LOX core/LH_2 annulus, and this results in a lower energy of mixing than if the propellants are reversed. The fact that satisfactory ignition was obtained with low energy mixing is encouraging. (Note, however, one unexplained delay of 100 m/s.) However, it is considered that the ignition with the coaxial stream injector would be even more reliable if an LH_2 core/LOX annulus flow pattern was selected. Objections on the grounds of adverse heat transfer effects would appear to be invalid following the recent significant study by Hersch.[8]

It is to be concluded that while the exact mechanism occurring at the injector face between the LOX/O_3F_2 and LH_2 is not yet known, mixing of hydrogen between 77° and 110° K with LOX/O_3F_2 results in hypergolic ignition at an ambient pressure of one atmosphere.

Future work is planned to closely define the temperature and pressure bounds within which satisfactory hypergolic ignition can be achieved with LH_2-LOX/O_3F_2.

[8] Hersch, Martin, Effect of Interchanging Propellant on Rocket Combustion Performance with Coaxial Injection, NASA TU D-2169, February 1964.

VIII GENERAL CONCLUSIONS

1. A new reactor developed for the production of O_3F_2 significantly increases production rate of O_3F_2.

2. The solubility of O_3F_2 in LOX has been measured. At 88°K it is 0.05% by weight; the temperature dependence of solubility has also been determined.

3. Neat ozone fluoride is nondetonable when tested with a standard donor in a 1-inch-diameter test cup.

4. The short term storage stability of the LOX/O_3F_2 solution appears adequate for most operational needs.

5. Hypergolic ignition has been achieved in combustion chambers maintained at liquid nitrogen temperature by using LOX/O_3F_2 and either gaseous or liquid hydrogen (ambient pressure).